UNIVERSITI PUTRA MALAYSIA

FABRICATION OF POLYPYRROLE-MCM41 NANOCOMPOSITES USING ELECTRODEPOSITION METHOD

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By

ROZITA YAHAYA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirement for the Degree of Master

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DEDICATION

I look up the hills,
Where does my help come from?
My help comes from Allah, the Almighty,
The creator of the whole universe, heaven and earth.

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of requirement for the degree of Master of Science

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April 2006

Chairman : Professor Anuar Kassim, PhD

Faculty : Science

Purely siliceous MCM-41 (SiMCM-41) and aluminium-containing MCM-41 (AlMCM-41) with different ratios of Al/Si were synthesized following a modified procedure of Ryoo and Kim (1995). Polypyrrole/MCM-41 (PPy/MCM-41) conductive polymer nanocomposite films was electrochemically prepared on Indium Tin Oxide (ITO) glass electrode from an aqueous solution of pyrrole monomer and *p*-toluene sulfonate dopant in a suspension of prepared MCM-41. Various PPy/MCM-41 nanocomposite films were obtained by varying the experimental conditions with the objective of producing conductive polymer nanocomposites with enhanced thermal and conductivity properties. The prepared nanocomposite films were characterized by Fourier Transform Infrared (FTIR) Spectroscopy, X-ray diffraction (XRD) analysis, Thermogravimetric Analysis, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and conductivity measurements. From observations of the XRD patterns, nanocomposites prepared at low Al/Si ratio (PPy/Al30 and PPy/Al40) and PPy/SiMCM-41 showed better crystallinity compared to those prepared at high Al/Si ratio (PPy/Al60 and PPy/Al80) which was observed to be amorphous. FTIR and XRD studies showed that the PPy and SiMCM-41 are the most compatible for the formation of PPy/SiMCM-41 nanocomposite. The TGA analysis and conductivity studies showed that the best nanocomposite was PPy/SiMCM-41 which was found to be the most thermally stable with the highest conductivity of 5.24 S/cm. This sample was obtained with optimum condition with 0.5 M pyrrole, 0.1 M *p*-toluene sulfonate and 3 g/dm^3 MCM-41 at 1.2 volt (vs SCE).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PEMBUATAN NANOKOMPOSIT POLIPIROL-MCM41 DENGAN KAEDAH PENYEDIAAN ELEKTROKIMIA

Oleh

ROZITA YAHAYA

April 2006

Pengerusi : Profesor Anuar Kassim, PhD

Fakulti : Sains

MCM-41 dalam bentuk silika tulen (SiMCM-41) dan MCM-41 yang mengandungi aluminium dengan nisbah Al/Si yang berbeza telah disintesis mengikut prosedur Ryoo dan Kim (1995) yang telah diubahsuai. Filem nanokomposit polimer pengalir bagi polipirol/MCM-41 (PPy/MCM-41) telah disediakan melalui kaedah elektrokimia di atas elektrod kaca Indium Stanum Oksida (ITO) daripada larutan akuas yang mengandungi monomer pirol, dopan *p*-toluena sulfonat dan larutan terampai MCM-41. Pelbagai nanokomposit filem PPy/MCM-41 diperolehi dengan pelbagai keadaan eksperimen dengan objektif untuk menyediakan nanokomposit polimer pengalir yang lebih stabil terhadap terma dan mempunyai sifat pengalir elektrik yang baik. Pencirian filem nanokomposit polimer pengalir PPy/MCM-41 yang telah disediakan telah dilakukan menggunakan infra merah transformasi Fourier (FTIR), pembelauan sinar-X (XRD), kajian terma, mikroskopi imbasan elektron (SEM), mikroskopi

pancaran elektron (TEM) dan penentukuran kekonduksian. Analisis daripada XRD, menunjukkan nanokomposit polimer pengalir PPy/SiMCM-41 dan PPy/MCM-41 dengan nisbah Al/Si yang rendah (PPy/Al30 dan PPy/Al40) adalah bersifat kristal berbanding dengan disediakan menggunakan nisbah Al/Si yang tinggi (PPy/Al60 dan PPy/Al80) adalah bersifat amorfus. Dari kajian FTIR dan XRD pula menunjukkan PPy dan SiMCM-41 adalah yang paling sesuai untuk pembentukan filem nanokomposit PPy/MCM-41. Dari kajian terma dan penentukuran kekonduksian, PPy/SiMCM-41 adalah nanokomposit yang terbaik dan paling stabil terhadap terma dengan nilai konduktiviti tertinggi iaitu 5.24 S/cm. Filem tersebut disediakan dengan larutan pirol berkepekatan 0.5 M, 0.1 M larutan *p*-toluena sulfonat dan 3g/dm^{-3} MCM-41 pada keupayaan 1.2 v (melawan SCE).

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I certify that an Examination Committee has met on 4^{th} April 2006 to conduct the final examination of Rozita Bt Yahaya on her Master of Science thesis entitled "Fabrication of Polypyrrole-MCM41 Nanocomposites using Electrodeposition Method " in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: 15 JUN 2006

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

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Date: 13 JUL 2006

DECLARATION

I hereby declare that the thesis is based on my original work except or quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

ROZITA BT YAHAYA

Date: 04 Ogos 2006.

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CHAPTER I

INTRODUCTION

Nanostructures Materials

The trend to smaller and smaller structures, that is, miniaturization, is well known in the manufacturing and microelectronics industries, as evidenced by the rapid increase in computing power through reduction on chips of the area and volume needed per transistor (Roher, 1993). Smallness in itself is not the goal. Instead, it is the realization, or now possibly even in the expectation, that the new properties intrinsic to novel structures will enable breakthroughs in a multitude of technologically important areas (Gleiter, 1989).

Of particular interest to materials scientists is the fact that nanostructures have higher surface areas than do conventional materials. The impact of nanostructure on the properties of high surface area materials is an area of increasing importance to understanding, creating and improving materials for diverse aplications. High surface areas can be attained either by fabricating small particles or clusters where the surface-to-volume ratio of each particle is high, or by creating materials where the void surface area (pores) is high compared to the amount of bulk support materials. Materials such as highly dispersed supported metal catalysts and gas phase clusters fall into the former category, and microporous (nanometer-pored) materials such as zeolites, high surface area inorganic oxides, porous carbons, and amorphous silicas fall into the latter category.

A focus of frontline interdisciplinary research today is the development of the conceptual framework and the experimental background of the science of nanostructured materials and the perspectives of its technological applications. We consider some current directions in the preparation, characterization, manipulation and interrogation of nanomaterials, in conjunction with the modeling of the unique structure-dynamics-function relations of nanostructures and their assemblies. The implications of quantum size and shape effects on the energetics, nuclear-electronic level sctructure, electric-optical response and dynamics, reveal new unique physical phenomena that qualitatively differ from those of the bulk matter and provide avenues for the control of the function of nanostructures. Current applications in the realm of nanoelectronics, nanooptoelectronics and information nanoprocessing are addressed and other directions highlighted. Chemical sciences make a central contribution to this novel and exciting scientific-technological area.

Nanoscience and nanotechnology pertain to the synthesis, characterization, exploration, interrogation, exploitation and utilization of nanostructured materials, which are characterized by at least one dimension in the nanometer (1 nm = 10^{-9}m) range. Such nanostructured systems constitute a bridge between single molecules and infinite bulk systems. Individual nanostructured involve clusters, nanoparticles, nanocrystals, quantum dots, nanowires and nanotubes, while collections of nanostructured involve arrays, assemblies and superlattices of individual nanostructured (Rao and Cheetham, 2001). Table 1.1 lists some typical dimensions of nanomaterials (Rao and Cheetham, 2001). The chemical and physical properties of nanomaterials can significantly differ from those of the atomic-molecular or the bulk materials of the same chemical composition. The uniqueness of the structural characteristics, energetics, response, dynamics and chemistry of nanostuctures is novel and constituent the experimental and conceptual background for the novel field of nanoscience. Suitable control of the properties and response of nanostructures can lead to new devices and technologies.

Perspectives in Nanoscience and Nanotechnology

The emerging nanoworld encompasses entirely new and novel means of investigating structures and systems. Species as small as single atoms and molecules will be manipulated and even exploited as atomic switches (Eigler *et al.*, 1997; Wada 1997). Computer-controlled scanning probe microscopy enables real-time, hands-on nanostructures manipulation. Nanomanipulators have been designed to operate in scanning and transmission electron microscope as well. A nanomanipulator gives virtual telepresence on the surface, with a scale factor of a million to one. Optical tweezers provide another approach to hold and move nanometer structures, a capability special useful in investigating dynamics of molecules and particles (Mehta *et al.*, 1999).

Table 1.1: Nanostructures and their assemblies (Rao and Cheetham, 2001)

Nanostructure	Size	Material
Cluster Nanocrystals Quantum dots	Radius: 1-10nm	Insulators, semiconductors, metals, magnetic materials
Other nanoparticles	Radius: 1-100nm	Ceramic oxides
Nanobiomaterials Photosynthetic reaction center	Radius 5-10nm	Membrane protein
Nanowires	Diameter: 1-100nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	Diameter: 1-100nm	Carbon, layered chalcogenides
Nanobiorods	Diameter: 5nm	DNA
2D arrays of Nanoparticles	Area : several nm^2	Metals, semiconductors, Magnetic materials
Surfaces and thin films	Thickness : 1-1000nm	Insulators, semiconductors
3D superlattices of nanoparticles	Radius: several nm	Metals, DNA Metals, semeconductors, magnetic materials

- Quantum structures, that is nanoparticles and nanocrystals of metals and of semiconductors, nanostructures, nanowires and nanobiological systems
- Assemblies of nanostructures (e.g., nanoparticles and nanowires) and the use of biological system (e.g., DNA) as molecular nanowires, as well as templates for metallic or semiconducting nanostructures
- Theoretical and computational studies that provided the conceptual framework for structure, dynamics, response and transport in

nanostructures. Theory and simulations in chemical sciences are unique in the building of conceptual bridges with experiment.

Questions such as "How does a polymer move, generates force, respond to an applied force and unfold?" can be answered by the use of optical tweezers (Weiss, 1999). It is noteworthy that the positioning of nanoparticles accurately and reliably on a surface by using the tip of an atomic force microscope as a robot has already been accomplished. Large-scale operation requiring parallel tip arrays is now being explored in several laboratories.

Novel potential developments in the realm of nanotechnology pertain to nanomaterials, molecular and biological nanomachines, biological and medical applications and environmental protection and improvement. Consolidated nanostructures employing both ceramic and metallic materials are being increasingly recognized as important in creating new generations of ultra high-strength, tough structural materials, new types of ferromagnets, strong and ductile cements and new biomedical prosthetics. Typical of the nanostructured hard materials are Co/WC and Fe/TiC nanocomposites. Nanoparticle-reinforced polymers are being considered for automotive parts. Several nanostructured alloys of high strength have been discovered and are in an advanced stage for use. Besides high-strength materials, dispersions and powders, as well as large bodies of novel morphologies, are being discovered. Coatings with highly improved features resulting from the incorporation of nanoparticles are being developed.